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consideration has been given to residence time effects, largely a result of delays in the onset of soot formation which reduces the effective time for soot growth. Additional work has emphasized the development of sampling and mass spectrometric measurement techniques for the measurements in particle laden regions. This work has resulted in the development of a new probe for conducting such measurements.

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Summary

The present research program is intended to provide a fundamental understanding of the processes controlling soot particle formation under conditions applicable to future gas turbine engine operation. During the current year of the effort, work has emphasized the effects of concentration and temperature on the formation of soot particles. Through a carefully structured study, the effects of adding a diluent to the fuel stream of a diffusion flame have been studied. Measurements and modelling efforts have shown that differences in the initial concentration of fuel are rapidly mitigated by diffusional processes. Consequently, local concentration variations are reduced between the initial undiluted and diluted flow cases. Furthermore, local temperature measurements indicate that even under equal adiabatic flame conditions, the local temperature in the soot forming region can differ by 40K between flames involving nitrogen or argon as the diluent. These differences in temperature are argued, based on previous work by other researchers, to be a possible source for the observed effects on soot formation. Additionally, consideration has been given to residence time effects, largely a result of delays in the onset of soot formation which reduces the effective time for soot growth. Additional work has emphasized the development of sampling and mass spectrometric measurement techniques for measurements in particle laden regions. This work has resulted in the development of a new probe for conducting such measurements.

1.0 Research Objectives

The primary objective of the present research program is to provide a fundamental understanding of the processes which control soot particle formation under conditions applicable to future gas turbine engine operation. The current work extends recent studies in laminar diffusion flames on the effects of fuel molecular structure and operating pressure. The emphasis in the present studies is to examine the important gas phase chemistry which is involved in particle inception and surface growth processes. The inception region is of particular interest because it has been argued to be controlling with respect to the ultimate amount of soot formed in the flame. This argument is based on the importance of the initial surface area formed during the inception of the primary soot particles. Present theories conflict on the importance of inception and surface growth in controlling the amount of soot formed during the combustion process. In the present studies, detailed measurements of both the inception and surface growth phases are being undertaken to provide the necessary basis for evaluating the relative importance of these fundamental mechanisms on the formation of soot particles.

One particular challenge for the present studies is the need to acquire data over a wide range of flame conditions. Additionally, information on both gas and condensed phase materials are required. Furthermore, the gas phase measurements must often be obtained in regions where particles are also present. Previous attempts to obtain spatially resolved species measurements in such situations have typically met with considerable problems due to particle related probe interferences, for example, clogging of microprobe orifices. Consequently, a concurrent objective of the present program has been the development of suitable measurement approaches needed to accomplish the objectives described above.

The current annual report will, thus, focus on two aspects of the previous year's accomplishments. The first relates to advances in our basic understanding of the processes important in soot formation. The second aspect will describe advances in the diagnostic capabilities which allow either measurements in two phase regions of the combustion environment or provide new information regarding our interpretation of measurements regarding the soot formation process.

2.0 Research Approach

The approach taken for the present research program is to undertake studies in a well controlled flame environment in which extensive measurement capabilities can be brought to bear. The flame system selected for study is a coannular laminar diffusion flame burning in air. This system has been selected for study for two reasons. First, it is the simplest non-premixed flame configuration which can simulate real combustion situations where mixing effects are important. Secondly, the flame configuration has been extensively investigated in the past in this and other laboratories. Consequently a solid data base exists from which to develop models as well as to assess the current needs for further research.

Recent studies supported by AFOSR in our laboratory have allowed measurements of several key properties of these soot forming flames. These measurements include determination of important soot particle properties such as volume fraction, diameter and number concentration. Complementary measurements of velocity and temperature have allowed mechanistic investigations of the important processes controlling soot formation, such as surface growth. Additionally, because of the detail and completeness of the studies, these measurements have proven of value to flame modelers, as well as to others who are involved with phenomena related to particles in chemically reacting flows. Examples of the later activities include developments related to fractal interpretations of light scattering measurements and the formation of titanium dioxide particles.

During the past year of this program, additional diagnostic capabilities have been developed to provide information on key soot processes. In particular, mass spectrometric sampling and analysis capabilities have been developed and applied to laminar diffusion flames. Related to this activity has been the development of a sonic quartz microprobe for sampling in particle laden flows. These techniques provide new capabilities needed to measure gas phase species in both the precursor and surface growth regions. In the particle diagnostic area, scanning and transmission electron microscopy has been developed to allow complementary measurements of primary particle size in soot aggregates. This technique has allowed information to be obtained in fuel rich regions concerning the possible presence of a liquid phase in the evolution of soot from large gas phase species to solid carbonaceous particles.

Currently, this extensive diagnostic capability is being applied to four significant aspects of the soot formation: the role of large aromatics in soot precursor formation, the identification of important surface growth species in the post inception particle region, the processes controlling the termination of soot particle growth, and the relative importance of concentration and temperature effects in laminar diffusion flames.

3.0 Research Accomplishments and Status of Work

3.1 Introduction

The accomplishments for the past year of the research program have focused on two major areas: the development of new diagnostic capabilities and extending our understanding of the relative effects of concentration and temperature on the soot formation process. The first of these accomplishments is critical to the pursuit of our objectives for the current year, while second is further refining our understanding regarding the key processes controlling the amount of soot formed. In the following sections, these key accomplishments will be described in more detail. The impact on work planned for the current year will then be addressed in the next section.

3.2 Diagnostic Developments

3.2.1 Sonic Probe Sampling

As mentioned above, the need to determine gas species concentrations in regions containing soot particles presents serious diagnostic challenges. In general, optical diagnostic techniques can measure only a limited number of species and in some cases can not be reliably applied in the presence of soot particles. Sampling probe techniques usually are limited by orifice clogging problems which can only be overcome by increasing the orifice dimensions at the sacrifice of spatial resolution of the measurements. To overcome the aforementioned orifice clogging problem, a novel sonic sampling probe has been developed and applied to a series of laminar diffusion flames containing various amounts of soot. A patent disclosure for this probe has been submitted and is presently in the evaluation stage regarding potential industrial interest. The details of the design and operation of this probe were recently presented at the Eastern Section Meeting of the Combustion Institute (1). A summary of the operation of the sonic probe along with the results of a set of comparisons obtained to validate its operation is given below.

The approach employed to prevent clogging of the probe orifice involves mechanically oscillating a wire through the orifice region using a spring loaded solenoid plunger whose driving circuit is electronically interrupted periodically (see Figure 1). The constant motion of the wire relative to the quartz tube is responsible for keeping the orifice open. For the present probe, the effective orifice is the annulus formed by an oscillating 380 μm diameter Nichrome wire of uniform cross section and the 400 μm diameter orifice in the quartz tube. Therefore, the effective orifice is equivalent to a 125 μm circular hole. The wire is soldered into a 1.59 mm (1/16 inch) tube which is attached to a spring loaded soft iron solenoid plunger. The solenoid is activated with a 24 volt power supply providing 0.3 amperes current. The solenoid circuit is interrupted with the aid of a mini relay which is activated by a regular series of 5 volt pulses from a function generator. When the solenoid circuit is complete, the solenoid retracts the soft iron plunger and consequently the wire is partially withdrawn. A small portion of the wire still extends beyond the orifice because a constant effective orifice size is desired. The inward motion of the plunger compresses the spring behind the plunger. When the mini relay interrupts the solenoid circuit, the compressed spring expands and returns the plunger and the wire to its original position. Thus, the wire can be made to oscillate through the

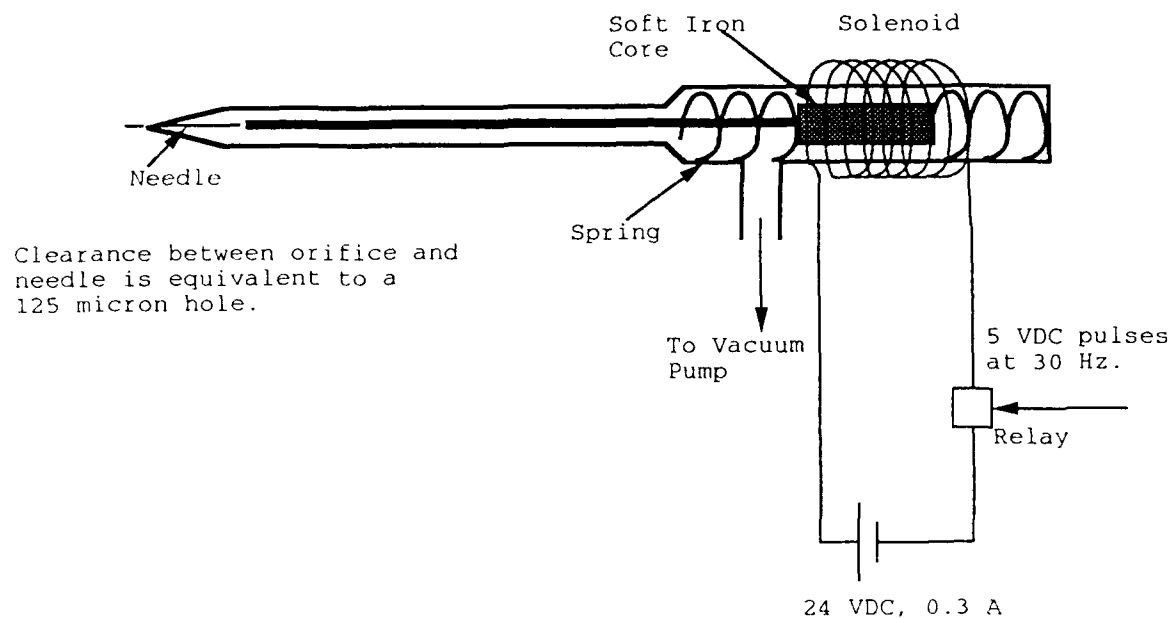


Figure 1. Schematic of Electromechanical Sonic Probe.

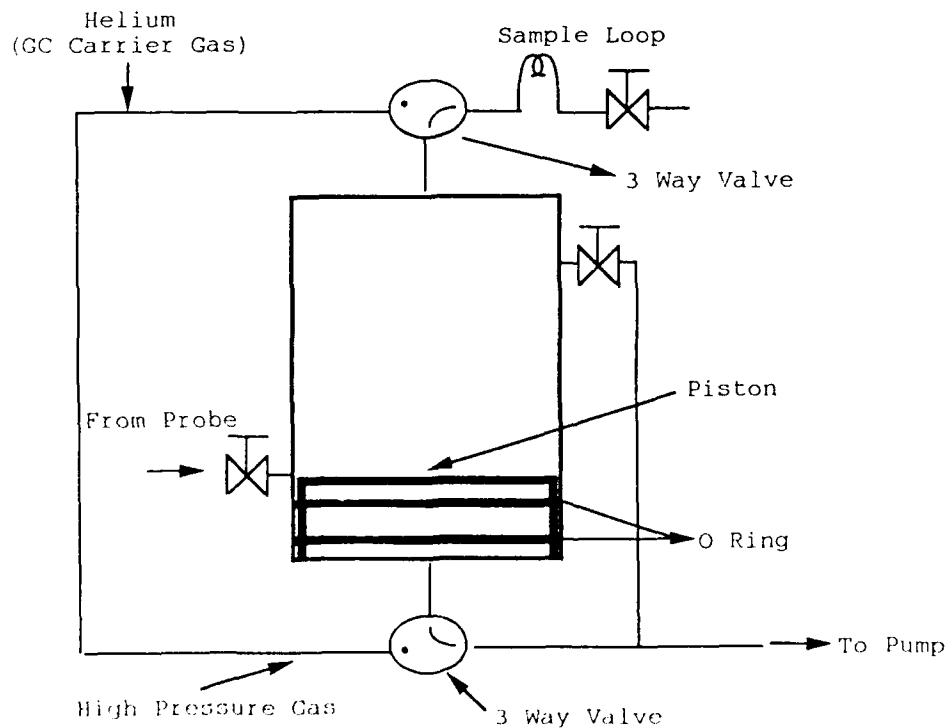


Figure 2. Schematic Of Sample Collection Apparatus

orifice region at the desired frequency. For the present system, an oscillation frequency of 30 Hz has been selected.

The operation of the probe was tested by sampling from a flame burning a mixture of methane (5.6 cm³/s) and 1-butene (1.05 cm³/s) in air (2.75 scfm) where the local soot volume fraction was 4.0×10^{-6} . Previous studies of this flame using a probe with a 1 mm diameter orifice resulted in clogging within 15 seconds under isokinetic sampling conditions. During initial testing, the pressure downstream of the probe was monitored as an indicator of clogging problems. The pressure remained constant at 5 torr for a period of 5 minutes indicating the probe did not clog during this time period. By manually blocking the probe orifice, it was established that should the probe clog, the pressure inside the probe would fall below 1 torr. To further validate operation of the probe, species measurements with gas chromatography were carried out in the flame described above. In order to use this low pressure sampling probe in conjunction with gas chromatography, a cylinder piston device (Figure 2) was designed and fabricated to compress the sample from 5 torr to 15 psi. The measurements from this probe were compared with results obtained from a water cooled stainless steel probe having a 2 mm orifice (which clogs within 5 minutes under isokinetic sampling conditions). Good agreement ($\approx 10\%$) is observed between the two probes for measurements obtained along the centerline from the upper regions of this flame. Figure 3 presents this comparison in a plot of CO mole fraction versus axial position in the flame. Other species also compare as well (data not shown). This probe was also compared with a conventional sonic probe (orifice 85 μm) in a relatively soot free methane flame and again the measurements compared well for the upper regions of the flame. However, some differences have been observed in the lower parts of the flame where steep concentration gradients are present.

In order to more closely examine these differences, a pure methane flame (CH₄: 5.7 cc/s, Air: 795 cc/s), that was previously studied by Mitchell (2), was selected. Radial particle measurements of the CO mole fraction at a height of 12 mm were made with three different probes – two conventional sonic probes and the electromechanical sonic probe (EMS). The probe orifice sizes were estimated by measuring the flow rate of room air through the probes under choked flow conditions. The EMS probe has the largest orifice with an equivalent circular diameter of 0.184 mm. The differences between various probe measurements that were observed in the lower part of the flame are related to the positioning uncertainty of the probe and differences in the spatial resolutions of each probe. In the lower region of diffusion flames, the species concentration gradients are steep on the air side of the flame front. Therefore, in this region uncertainties in probe positioning and differences in spatial resolutions have to be kept in mind when making comparisons. The effect of the finite probe orifice diameter results in "broadening" or decreasing the steepness of the species gradient and will be referred to as "gradient broadening".

Figure 4 compares the radial measurements of CO mole fraction with the three different probes. Since complete radial profiles across the entire flame were not obtained, some uncertainty in the location of the centerline of the flame exists. In order to examine the probe orifice effects on gradient broadening, the data in Figure 4 are shifted slightly to provide an overlap of the region of steepest gradient for each data set. For

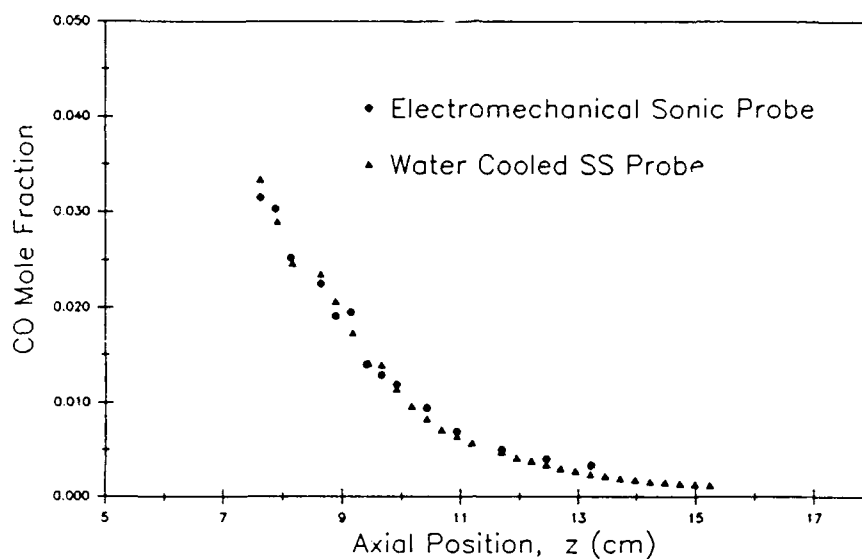


Figure 3. Comparison of CO measurements from the Electromechanical Sonic Probe with similar measurements from a water cooled stainless steel probe.

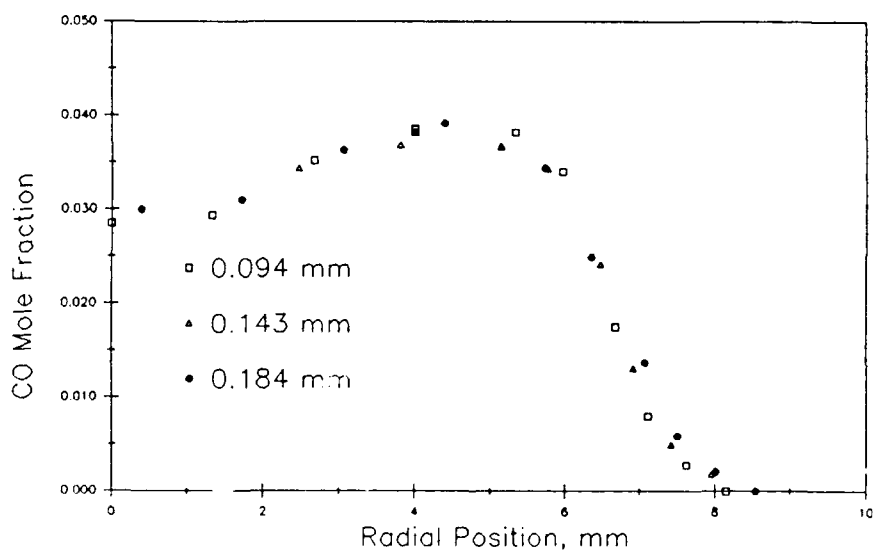


Figure 4. Radial profiles of CO mole fraction from probes with three different orifice sizes demonstrate gradient broadening. The symbols identified on the plot refer to the orifice diameters.

the region between the centerline and the peak CO mole fraction location, there is no significant difference between the measurements from the three probes. On the air side of the peak CO mole fraction, the probe with the smaller orifice gave CO values displaying steeper radial gradients. This is understandable since a smaller orifice results in better spatial resolution and less gradient broadening.

For the present EMS probe, a nichrome wire is used to keep the orifice of the probe open. Attempts at using a quartz fiber have not been successful, since this fiber becomes brittle once it is exposed to the flame and breaks easily. Since the measurements from the probe with the nichrome wire compare well with measurements using the other probes, this probe has been used to obtain radial profiles of gas phase species in the sooty regions of the flames currently under study. Some concerns remain about potential catalytic effects due to the nichrome wire and must be considered as the EMS probe is used in other environments.

Table 1 indicates the fuel and air flow rates for the profiles studied with the various probes. While figures 5 and 6 show typical radial profile measurements of N_2 , CO_2 , O_2 and CO in these flames. The symbols represent actual measurements and the lines through the symbols are extended across the flame centerline by symmetry. Fuel species measurements and moisture estimates are not plotted. Present efforts are aimed at applying the EMS probe in conjunction with the quadrupole mass spectrometer system which has been assembled for studies of the soot precursor and surface growth zones. Initial use of the EMS probe with the gas chromatographic system has provided a solid analysis technique for comparisons with the mass spectrometer results. The availability of complementary measurement capabilities (gas chromatography and mass spectrometry) provides an increased level of assurance as these techniques are applied to new flame environments.

The above discussion summarizes the status and progress achieved regarding development and validation of the intrusive probe sampling system. Although continued improvements are anticipated the present system does provide the necessary capabilities to obtain the measurements required for the current research program. Efforts aimed at applying the EMS probe in conjunction with the quadrupole mass spectrometer system which has been assembled for studies of the soot precursor and surface growth zones are presently underway.

Table 1: Fuel and air flow rates (cm^3/s) for the overventilated flame studies

FLAME	CH_4	C_4H_{10}	C_4H_8	AIR
Pure Methane	9.8	--	--	1298
Methane/Butane	5.6	1.05	--	1298
Methane/1-Butene	5.6	--	1.05	1298
Mitchell	5.7	--	--	795

3.2.2 Mass Spectrometric Analysis for Laminar Diffusion Flames Measurements

A quadrupole mass spectrometer system (ms) has been assembled for measurement of gas phase species in the laminar diffusion flames presently under study. Samples obtained from the flame using an

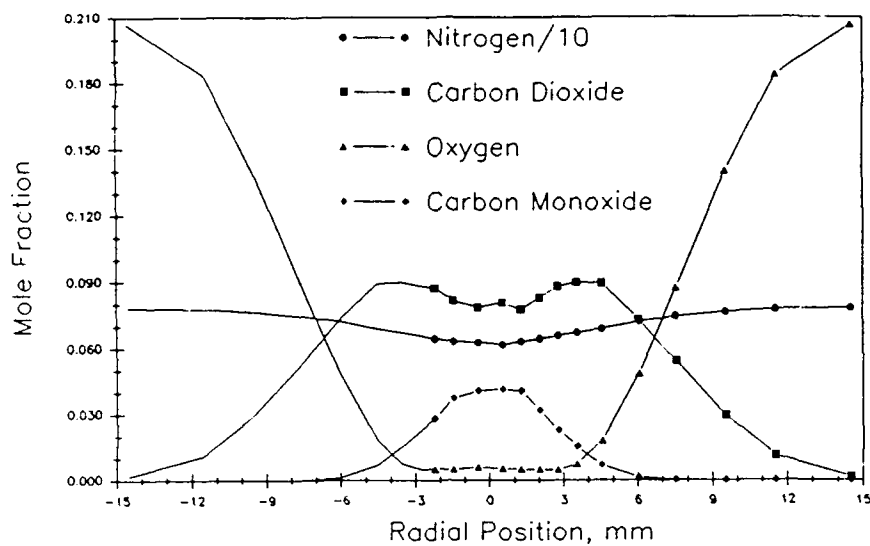


Figure 5. Radial profiles of N_2 , CO_2 , O_2 and CO in the pure methane flame at a height of 7.874 cm.

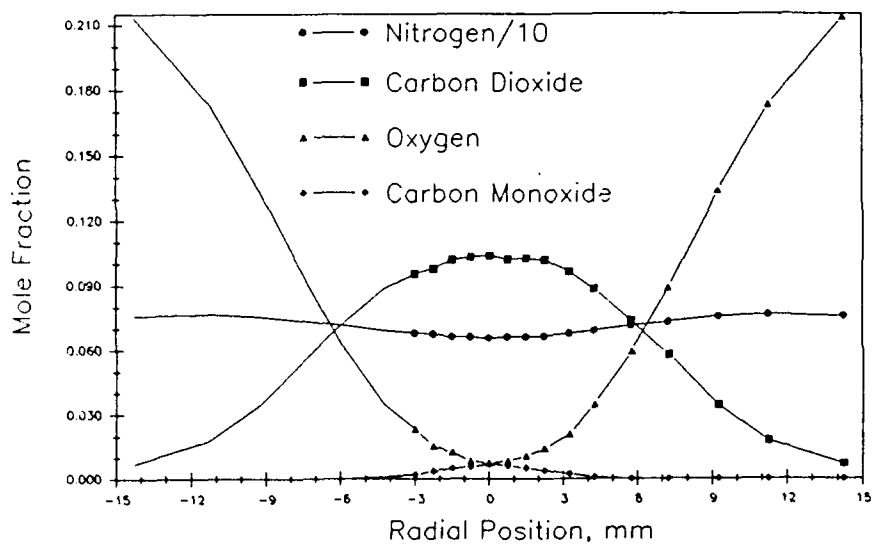


Figure 6. Radial profiles of N_2 , CO_2 , O_2 and CO in the pure methane flame at a height of 9.906 cm.

appropriate quartz sampling probe, can be analyzed according to their mass number using this instrument. Similar probing of non-soot containing regions of Wolfhard-Parker flames have been previously reported by Smyth et al. (3). However, as described above, measurements in particle laden regions have been limited by probe clogging problems. This facility was obtained under support of AFOSR through a DoD University Research Instrumentation Award.

Studies during the past year have focused on developing our mass spectrometer skills in relatively soot free flame environments using conventional quartz microprobe approaches. These studies have been used in conjunction with studies of concentration and temperature effects to be described in the next section. Figures 7 and 8 show species measurement results for two methane flames burning in air. In each flame, the methane fuel flow rate was $5.7 \text{ cm}^3/\text{s}$ and the measurements were obtained for a height 12mm above the lip of the burner. In order to investigate the effect of fuel concentration and temperature on the soot formation, dilution of the methane flow with nitrogen was employed to vary fuel concentration. Figure 7 shows the results for an undiluted methane flame while Figure 8 is for a 50% diluted case. Measurements are presented for a number of combustion products (H_2O , CO_2 and CO) as well as for the fuel and some intermediate species such as H_2 and C_2H_2 . Of course C_2H_2 is a species of special interest because of its potential importance in the soot surface growth process.

From a diagnostic viewpoint, these results demonstrate the capabilities of the present probe/mass spectrometer system to provide spatially resolved species measurements for the current laminar flame studies. Comparisons with measurements obtained with the previously mentioned gas chromatograph system have been quite good. This agreement assures that the calibration procedure used with the mass spectrometer system is providing accurate measurement results. Further discussion of these results, with respect to the fuel dilution studies, will be addressed in the next section.

Current experiments are incorporating the EMS sonic probe approach into the mass spectrometer system to allow measurements in soot laden regions. Recent work has also examined the high mass measurement capabilities of the system. Masses as high as 178 amu (atomic mass units) have been observed and included important aromatic hydrocarbons such as acenaphthylene (152 amu). Our studies indicate measurements of higher mass species appear to be feasible with the use of phase sensitive detection approaches. An appropriate chopper for the mass spectrometer system is presently being acquired to allow these higher mass species measurements. Measurements of high mass species have also been attempted using a wavelength selective optical absorption technique. Although extremely sensitive (five parts in a thousand) absorption measurements were obtained in the coannular flames, uncertainties in the value of index of refraction of the early primary soot particles has made quantitative species measurements not feasible for the large precursor species. The presence of soot particles contributes to the overall absorption measurements which must be subtracted as a background effect in order to determine the contribution from gas phase molecules. Additionally, the short optical path length available in the coannular flame configuration limits the optical absorption technique as well. Presently, alternative approaches are being considered, including the use of

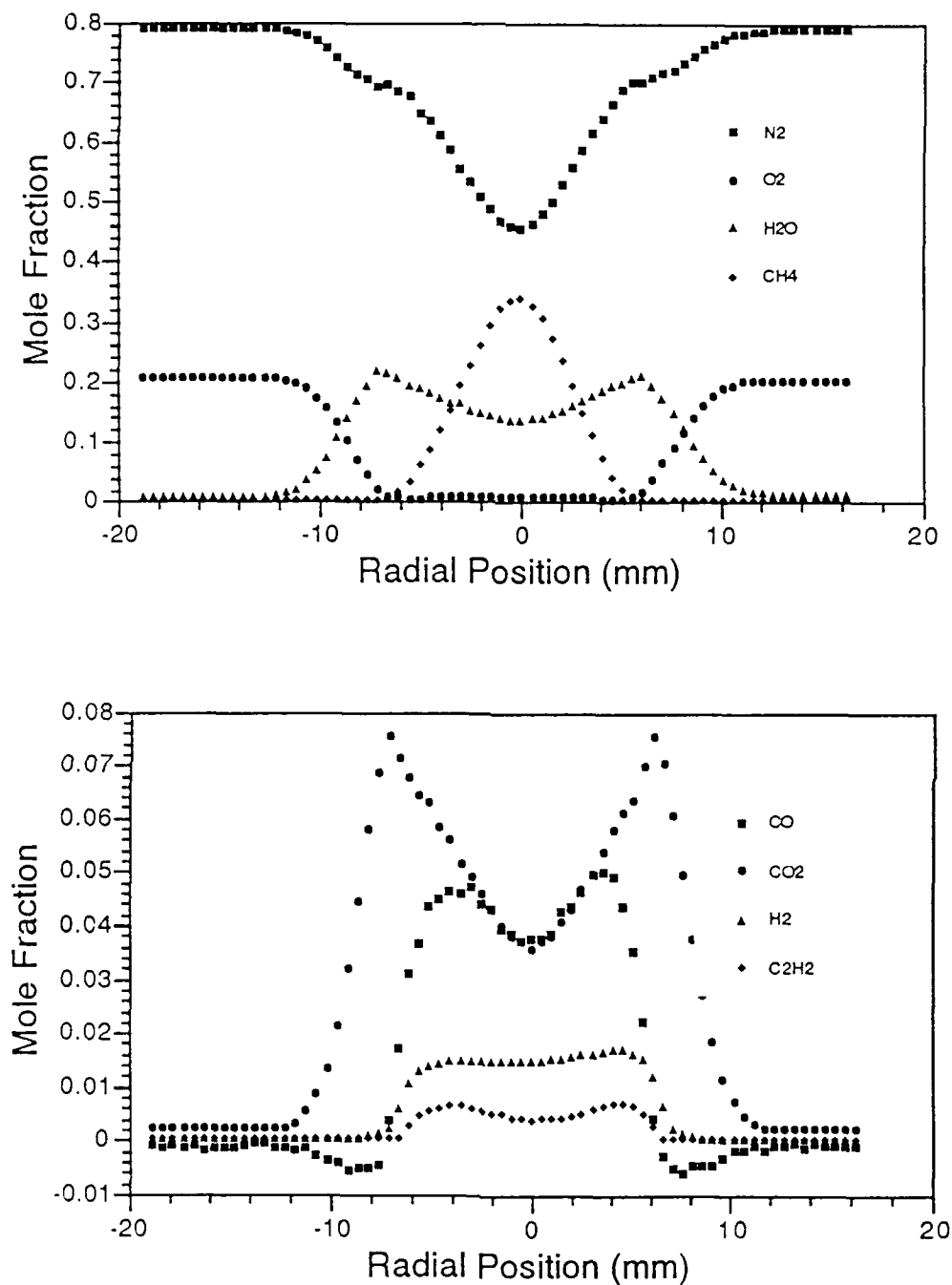


Figure 7. Mole fraction measurement as a function of radial position in an undiluted methane diffusion flame burning in air. The axial measurement location is 12 mm above the burner exit. Note negative mole fraction measurements for CO are a result of obtaining CO mole fractions from a differencing procedure involving the mass 28 peak which includes both CO and N_2 . The methane fuel flow rate was $5.7 \text{ cm}^3/\text{s}$.

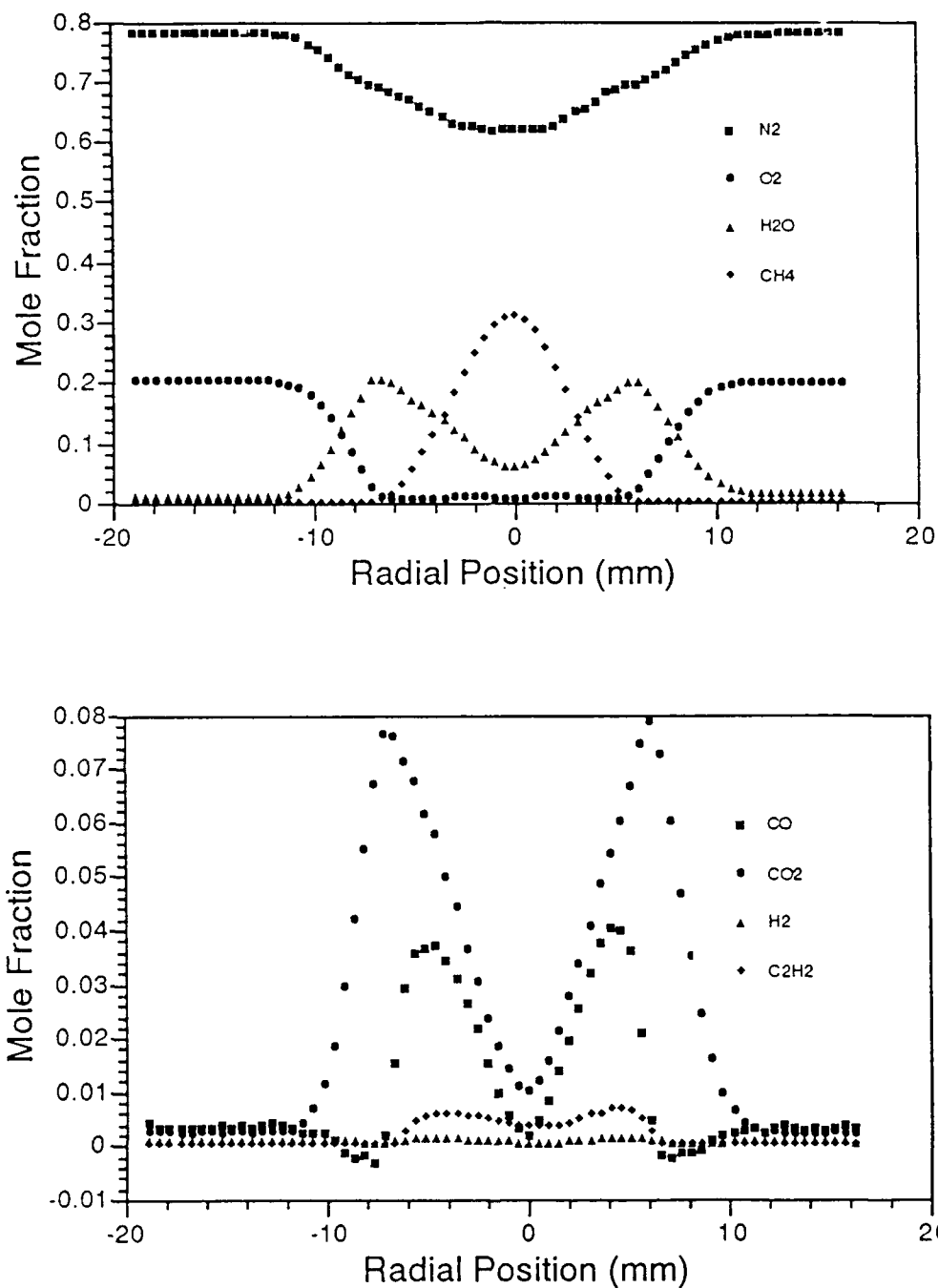


Figure 8. Mole fraction measurement as a function of radial position for a 50% N₂ diluted methane flame burning in air. The axial measurement location is 12 mm above the burner exit. Note negative mole fraction measurements for CO are a result of obtaining CO mole fractions from a differencing procedure involving the mass 28 signal which includes both CO and N₂. The methane and nitrogen fuel flow rate were each 5.7 cm³/s.

other flame geometries such as Wolfhard Parker and underventilated coannular diffusion flames in order to investigate the evolution of large hydrocarbon species which serve as soot precursors.

3.3 Soot Formation Studies of Fuel Dilution Effects

3.3.1 Background

The formation of soot particles in combustion environments involves a complex series of chemical and physical processes which control the conversion of fuel carbon to carbonaceous particles. Since soot formation is well known to be a chemically kinetic limited process, the effects of temperature and concentration are expected to be important. In the case of concentration effects, it would seem straightforward to expect a direct proportionality between fuel concentration and soot formation rates. However, in many situations, mixing and temperature effects can mask the importance of the fuel concentration variations on the amount of soot formed in the combustion environment.

One means to investigate the effect of fuel concentration is through the introduction of an inert diluent into the fuel stream. Diluting the fuel stream has been observed to reduce soot concentration in laminar diffusion flames (4). This reduction is in part a result of lower flame temperatures achieved in diluted flames as compared to the undiluted case. These lower temperatures reduce the pyrolysis reaction rates leading to decreased soot formation rates and consequently lower soot concentrations. Reducing the fuel concentrations may have an effect on soot concentration through a proportional reduction in fuel species concentration in the soot formation region, i.e. reaction rates are decreased by lower species concentration. During the past year, a study of the effect of fuel dilution has been undertaken with the objective of further refining our understanding of the effects of concentration and temperature. As part of this study the effects of other parameters such as residence time have also been considered in the analysis.

Although reduction in soot through inert addition has been observed by numerous researchers, only a few studies exist which investigate the relative roles of fuel concentration and flame temperature. Previous studies of laminar diffusion flames have employed dilution as a means to study temperature effects on soot formation (5,6). In these cases the effects of dilution were argued to be small relative to the temperature reduction contribution. Kent observed that soot concentrations in diluted flames are reduced by an amount that can not be explained by the reduction in flame temperature alone (7). Axelbaum and Law addressed this issue in a series of experiments in counterflow flames (8,9). The important conclusion from these studies is that soot formation rates depend linearly on the initial fuel concentration. Axelbaum and Law recently extended their dilution studies to include coflow diffusion flames (10). They report a dilution effect for coflow flames that is consistent with the counterflow flame results; that is, the maximum soot volume fraction increases linearly with respect to the fuel concentration at the burner exit. These results imply that the role of temperature in soot formation, commonly believed to be the governing parameter of soot formation rates, is in some situations less important than fuel concentration.

3.3.2 Experimental Setup and Operating Conditions

Investigating the role of temperature and concentration on soot formation requires a careful selection of

the experimental approach. Following a method similar to the approach of Axelbaum and Law (10), dilution is studied through a series of flames at identical calculated adiabatic flame temperatures, but which have different initial fuel concentrations. The difference in heat capacities of Argon and Nitrogen permit comparison of flames with identical temperatures, but different dilutions. Therefore, the effect of concentration is systematically isolated from temperature. Similarly, flame conditions can be selected with identical dilutions, e.g. 50% N₂ and 50% Ar, but different temperatures, thus, isolating the effect of temperature on soot formation. Desired flame conditions are calculated with the NASA Chemical Equilibrium Code (11) based on the assumption that the temperatures in the formation region of laminar diffusion flames scale with calculated adiabatic temperatures.

An atmospheric coannular burner was used to study laminar diffusion flames burning ethene or propane. A laser scattering/extinction system was used to obtain data on the soot particle field in these flames. The burner and light scattering apparatus has been previously described in the literature (12) and will be only briefly described. The coannular burner consists of an inner brass fuel tube (1.1 cm id) surrounded by an outer tube (10.0 cm id) for the air flow. The fuel or fuel inert mixture is burned in a highly over-ventilated air flow, minimizing the effect of airflow rate (13). Fuel flow rates are monitored on rotameters, while air flow rates are determined with a mass flow meter. Fuel gases had a stated purity of 99.5% and 99.0% for ethene and propane, respectively. Air was supplied from an in-house compressor which was filtered to remove particles and moisture. The air flow rates for the flames studied was 2.25 SCFM. Table 2 summarizes the flow conditions, which span a range of flow rates, dilutions, and temperatures.

The laser light extinction/scattering apparatus used a 4W argon ion laser operating at the 514.5 nm laser line. The laser source was modulated using a mechanical chopper operating at 1 kHz to allow for synchronous detection of the transmitted light signals. The laser beam is focused into the burner using a 40 cm focal length lens. The laser was typically operated with an output power of 0.5W. The transmitted light was detected using a silicon photodiode with the output of the detector input to a two phase lock-in amplifier which was interfaced to an IBM-XT computer. Laser light scattering measurements at a scattering angle of 90° with respect to the incident beam could also be obtained with this system. However, in the present experiments such measurements were only used for comparisons with previous studies. Since these measurement are not used in the present results, this part of the system will not be described in detail.

The entire atmospheric burner was mounted on a three-dimensional translating stage system. Computer controlled stepper motors were used to adjust the vertical and one of the horizontal coordinates. This allowed radial profiles of the laser extinction to be achieved at various axial positions in the flame.

Experiments at elevated pressures provide an alternative method for investigating fuel concentration effects on soot formation. The fuel and oxidation partial pressures are linearly related to the ambient pressure inside the vessel. Thus, increasing the pressure inside the vessel from 0.1 to 0.2 MPa (1 to 2 atmospheres) effectively doubles the molar concentration. A separate high pressure diffusion flame facility is composed of a pressure vessel, coannular burner, two-dimensional translating system, and gas metering apparatus. The

Table 2
Fuel Dilution Studies: Flow rate conditions, calculate flame temperatures and maximum
integrated soot volume fraction results

Flame #	Fuel (Q) (cm ³ /s)	Diluent	X _{Fuel}	T _{ad} (K)	F _v /c(λ,m)	Percent Change
1	C ₂ H ₄ (2.75)	N ₂	0.50	2310	0.0244	46.7
2	C ₂ H ₄ (2.75)	Ar	0.37	2310	0.0155	29.6
3	C ₂ H ₄ (4.90)	N ₂	0.50	2310	0.0429	51.8
4	C ₂ H ₄ (4.90)	Ar	0.37	2310	0.0312	37.7
5	C ₂ H ₄ (4.90)	N ₂	0.74	2346	0.0722	87.2
6	C ₂ H ₄ (4.90)	Ar	0.64	2346	0.0672	81.2
7	C ₂ H ₄ (4.90)	N ₂	0.64	2333	0.0602	72.7
8	C ₂ H ₄ (4.90)	Ar	0.52	2333	0.0556	67.2
9	C ₂ H ₄ (6.58)	N ₂	0.64	2333	0.0781	74.5
10	C ₂ H ₄ (6.58)	Ar	0.52	2333	0.0660	63.0
11	C ₂ H ₄ (2.75)	--	1.00	2369	0.0522	100.0
12	C ₂ H ₄ (4.90)	--	1.00	2369	0.0828	100.0
13	C ₂ H ₄ (6.58)	--	1.00	2369	0.1047	100.0
14	C ₃ H ₈ (2.56)	N ₂	0.61	2240	0.0392	79.8
15	C ₃ H ₈ (2.56)	Ar	0.50	2240	0.0362	73.7
16	C ₃ H ₈ (2.56)	--	1.00	2266	0.0491	100.0

High Pressure Flame Studies

Experiment #	Fuel (Q) (cm ³ /s)	Diluent	Pressure (atm)	X _{Fuel}	T _{ad} (K)	F _v /c(λ,m)
17	C ₂ H ₄ (3.85)	--	1	1.00	2369	0.0767
18	C ₂ H ₄ (3.85)	Ar	2	0.50	2351	0.0959
19	C ₃ H ₈ (2.56)	--	1	1.00	2260	0.0490
20	C ₃ H ₈ (2.56)	Ar	2	0.50	2258	0.0780

$$\text{Percent Change} = (F_v/c(\lambda,m)/(F_v/c(\lambda,m))_{\text{pure}}$$

pressure vessel consists of two sections of pipe. The lower section which is 20.32 cm (8 inches) in diameter, provides room for the vertical translation system as well as access for fuel and electrical lines. The upper section, which is 15.24 cm (6 inches) in diameter and 76.20 cm (30 inches) in length provides optical access for scattering and extinction via four 5.08 cm (2 inch) diameter, 1.27 cm (0.5 inch) thick windows. Vertical burner translation is provided by a stepper motor mounted inside the pressure vessel, while horizontal motion is provided by a stepper motor/ball bearing translating stage combination mounted externally. The burner consists of two concentric tubes of the same diameter as used in the atmospheric burner, however, the inner fuel tube is made of stainless steel. This degree of similarity between the atmospheric burner and high pressure flame facility allow comparisons between the two systems. Mass flow meters and controllers were used to maintain the gas flow rate constant independent of the operating pressure.

Rapid insertion thermocouple measurements provide measurements of the temperature distributions in the flames studied. The rapid insertion thermocouple technique avoids continuous coating with soot by burning off soot formed on the thermocouple surface in the oxidation zone of the flame. Pt/Pt-10% Rh fine wire thermocouples were made from 125 μm diameter wire. The resulting bead diameter was typically 160 μm . The uncoated thermocouples are mounted on a stepper motor stage for quick positioning. This technique provides accurate measurements of relative changes in the temperature as diluent species and concentrations are varied.

3.3.3 Analysis

In the present study, the quantity of interest is the change in soot volume fraction, f_v , resulting from dilution of the fuel. In previous studies of laminar diffusion flames, tomographic reconstruction approaches have proved useful in providing spatially resolved measurements of f_v from line-of-sight extinction measurements. In the present case, however, the errors associated with the tomographic reconstruction approach detract from its usefulness since small variations in the f_v need to be measured.

An alternate approach is to relate the extinction measurement to an appropriate spatial integral of the soot volume fraction. For soot particles in the Rayleigh size limit ($d/\lambda \ll 1$) the extinction (I/I_0) is related to f_v as:

$$\int_{-\infty}^{+\infty} f_v dx = -c(\lambda, m) \ln \left(\frac{I}{I_0} \right) \quad (1)$$

where x is the direction along which the laser beam propagates, $c(\lambda, m)$ is a constant determined from Rayleigh theory and x is the path length through the flame. A measure of the total integrated soot volume fraction, F_v , can be obtained by integrating equating (1) along the direction perpendicular to x . This integrated volume fraction is a measure of the total amount of soot at a particular axial location and is given by

$$F_v = - \int_{-\infty}^{+\infty} c(\lambda, m) \ln \left(\frac{I}{I_o} \right) dy \quad (2)$$

where y is the direction perpendicular to x and $c(\lambda, m)$ is a constant. The integrated volume fraction, F_v , has been selected because it incorporates any changes in flame diameter as the flow rate is varied.

3.3.4 Results

These studies address four aspects of the influence of inert additives on the reduction in soot formation: 1) the relation between the degree of dilution and soot reduction; 2) fuel flow rate effects; 3) potential fuel structure effects and 4) results at elevated pressure providing an alternate means of examining the role of concentration on the soot formation process. Using the information from these experiments, the relative influence of fuel concentration and temperature are considered for coflowing laminar diffusion flames.

The approach used to determine the relation between the degree of dilution (i.e. fuel concentration) on soot formation involved comparing argon and nitrogen diluted flames having the same calculated temperature. Since argon and nitrogen have different molar heat capacities, the initial fuel concentration of these flames must be different if the temperature is to be maintained constant. To ensure that the differences in soot formation rates in these flames of equal temperature are a result of differences in fuel concentration and not temperature, the temperature field was determined from rapid insertion thermocouple measurements. In addition, these measurements allowed a determination of whether calculated adiabatic temperatures may be used to represent the changes in temperature expected with dilution. This may not be self evident since calculated adiabatic temperatures are based on the fuel/diluent mixture being supplied to the burner and not the local concentration of the flames.

Thermocouple measurements were made in 4.90 cm³/s ethene flames (see Table 2) for fuel/diluent flow conditions that correspond to calculated temperatures of 2369K (flame 12), 2346K (flames 5 and 6) and 2333K (flames 7 and 8). The two lower temperature conditions were established individually for nitrogen (flames 5 and 7) and argon (flames 6 and 8) diluents. Uncorrected measured temperatures are shown in Figure 9 for an undiluted and diluted flame (flames 12 and 7) and indicate that the adiabatic flame temperature is not achieved. This observation is a result of two factors. First, the thermocouple measurements were not corrected for radiative losses. Second, temperatures in sooting flames are lower than calculated adiabatic values because of radiation losses from the soot particles as well as effects of conduction and finite chemistry (14). The radial temperature profiles of flames 12 and 7, shown in Figure 9 as a function of axial position, reveal a trend expected in the temperature. At axial heights less than 50mm, temperatures are reduced in the diluted flame, while above 50mm, the diluted flame has a higher temperature. The explanation for this observation lies in the fact that more soot is being formed in the initially hotter undiluted flame, increasing radiative losses, thus cooling the flame to a greater extent (6,7).

Careful inspection of the temperature profiles reveals that low in the flame, dilution reduces temperatures at the centerline to a greater extent than in the annular region (14). This difference in the

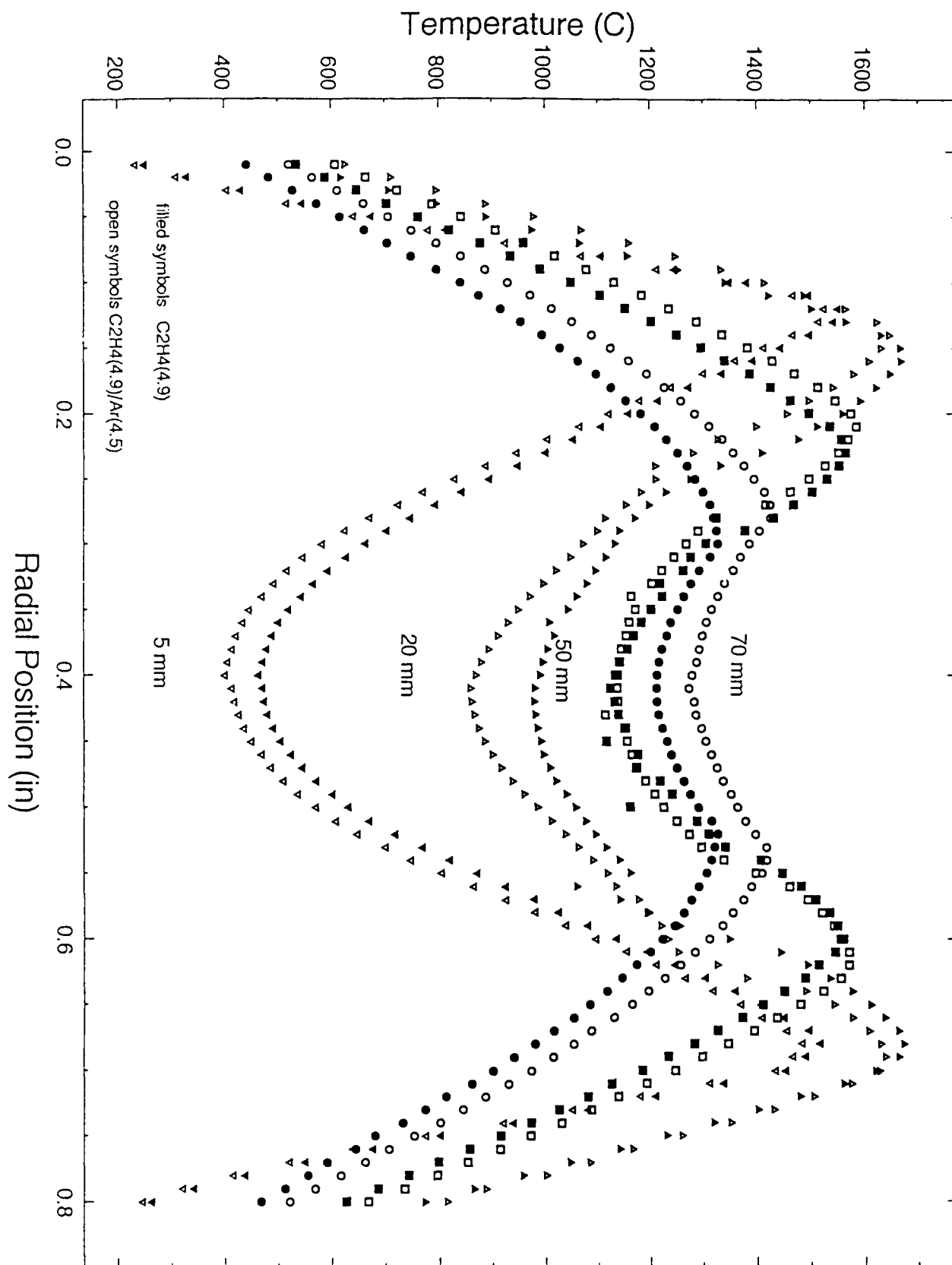


Figure 9. Uncorrected thermocouple measurements of the temperature profiles as a function of radial position for several axial heights in an undiluted and diluted ethene diffusion flame. The ethene fuel flow is $4.9 \text{ cm}^3/\text{s}$ while the argon diluent flow rate is $4.5 \text{ cm}^3/\text{s}$.

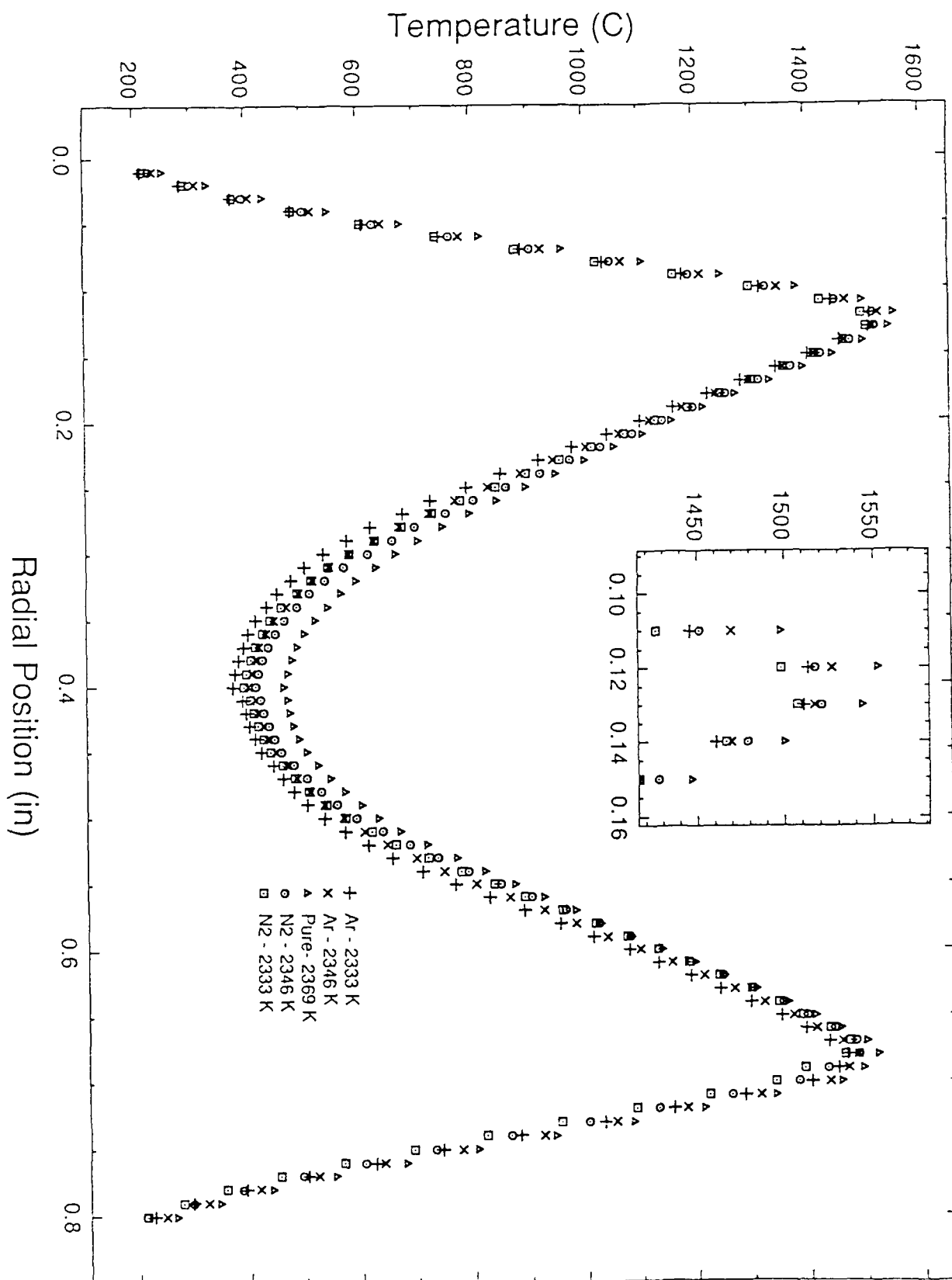


Figure 10. Comparison of uncorrected thermocouple measurements of the temperature profile at an axial height of 5mm as a function of radial position. Results are presented for an undiluted ethene flame and two pairs of diluted flames which have identical calculated adiabatic flame temperatures.

effect of the diluent as a function of position is related to the diffusional nature of these flames. For both the N_2 and Ar diluent cases, N_2 from the air stream is diffusing towards the centerline while the "fuel" (diluted or undiluted) diffuses towards the flame front. This interdiffusional aspect of the flame tends to mitigate the initial fuel concentration differences resulting from the addition of the diluent species. This point will be discussed in detail later.

In the annular region, low in the flame (5mm axial location), the measured temperature differences are similar to the differences in calculated adiabatic flame temperatures (see Figure 10). Flames in which diluent conditions are chosen to match the temperature show temperatures which differ by less than 10K in the region near the temperature maximum. As the centerline is approached from the maximum temperature location, differences between the N_2 and Ar diluted flames for identical calculated adiabatic flame conditions increase with the N_2 diluted flames having slightly higher temperatures. In the region where soot is formed this difference can be as large as 40 to 60K. Positioning uncertainty with respect to the thermocouple measurement location is not believed to be the source for these observed differences, since both the centerline minimum and the symmetric temperature maximums in the annulus show good positional agreement for each of the flames (see Figure 10). These observations underscore the need to consider the local temperature and concentration, as well as the overall expected behavior of the flame in assessing the effects of fuel dilution.

One of the goals of this investigation is to determine the variation in soot formation rates with the initial fuel concentration. This is most easily achieved by comparing the soot yield in flames of similar temperatures but different dilutions. A study of the soot formation in a set of three pairs of flames, each pair at a different temperature, is intended to address this issue. The variation in the integrated soot volume fraction, F_v , at various axial locations is shown in Figures 11 and 12 for each of the ethene flames with a flow rate of 4.90 cm^3/s . It is interesting to note that, although addition of diluent increases the burner exit velocities, the height at which the peak volume fraction is reached is nearly constant in these flames with possibly the exception of flame 4 which has the highest dilution. The height at which the soot maximum is reached is determined by the location at which oxidizer replaces the fuel at the centerline of the flame (15). Thus, the rate of diffusion of oxidizer into the flame front is only weakly dependent on the amount of fuel dilution.

The peak integrated soot volume fraction is used as a readily determined measure of the sooting propensity of these flames. The reduction in soot formed, shown in Table 2, is calculated from the peak F_v values. In this comparison, the reduction in soot may be due to both temperature and/or concentration. Peak soot concentration ratios show that reducing fuel concentration and temperature reduces the amount of soot formed. The flames which show the largest relative reduction in soot (flames 3 and 4), the most diluted flames, show a dependence on the soot formation rate which is directly proportional to the fuel concentration. This implies soot formation rates vary with concentration in less than a 1 to 1 linear manner, since the temperature reduction effect on soot formation has not been taken into account.

In order to quantify the effect of fuel concentration on the soot formation rates, the integrated soot

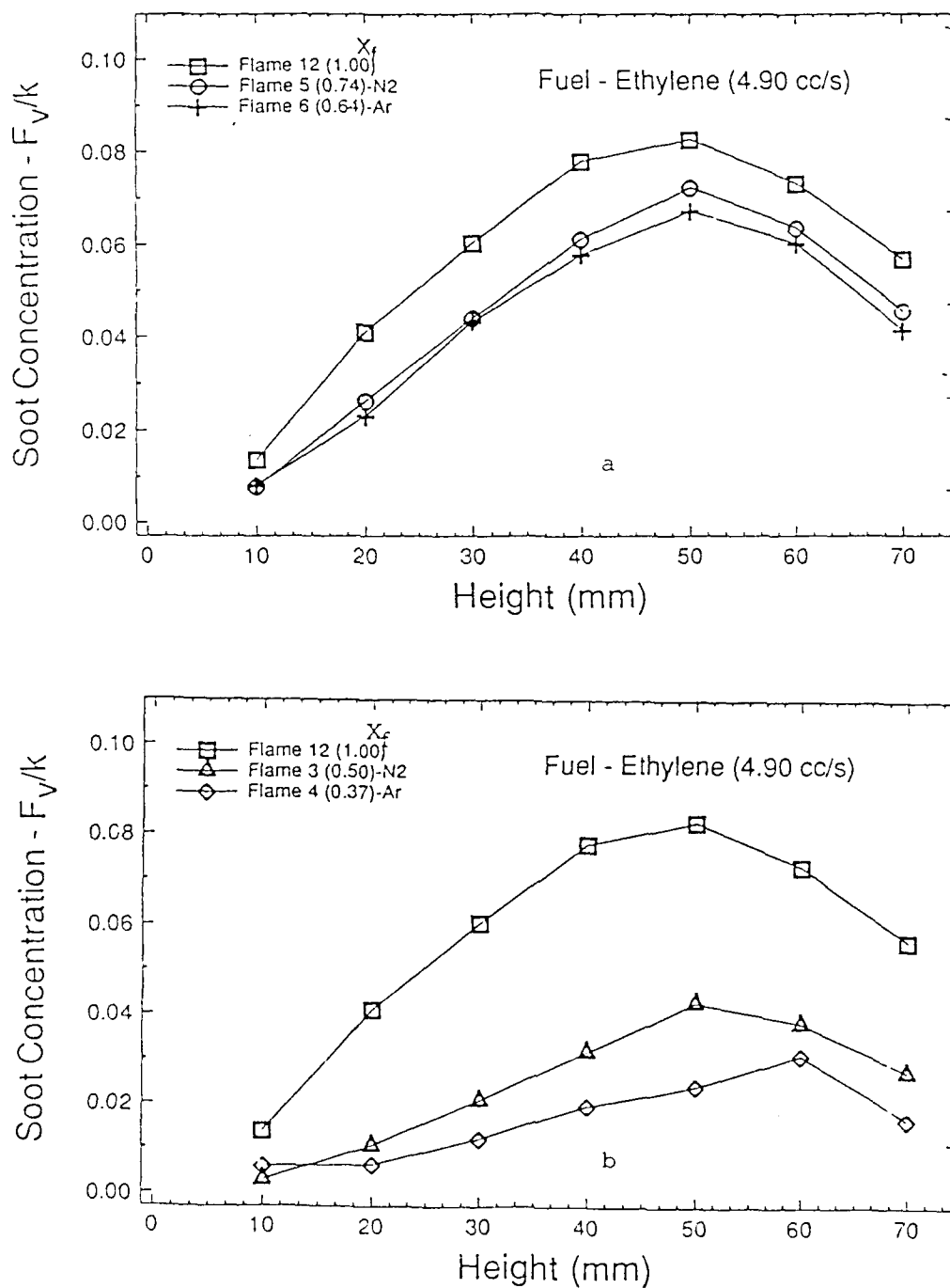


Figure 11. Comparisons of the integrated soot volume fraction as a function of height for diluted ethene flames of equivalent temperature as compared to an undiluted flame (flame 12).
a) flames 5 and 6 b) flames 3 and 4. In this figure, $k = c(\lambda, m)$.

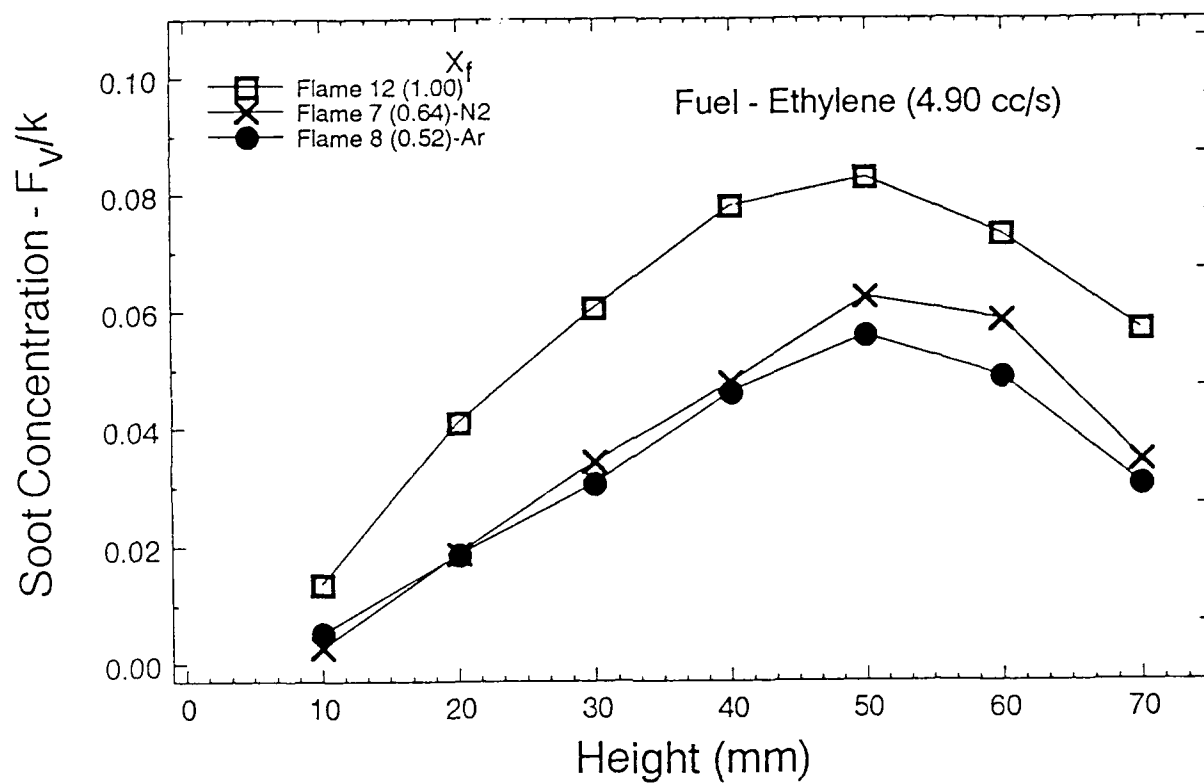


Figure 12. Comparison of the integrated soot volume fraction as a function of height for diluted ethene flames of equivalent temperature as compared to an undiluted flame (flame 12). This figure is for flames 7 and 8. In this figure, $k = c(\lambda, m)$.

volume fraction, F_v , was taken to be related to the initial fuel concentration by:

$$F_v \propto [\text{Fuel}]^b \quad (3)$$

From the measured differences in F_v for the argon and nitrogen cases, a value for b can be obtained and is shown in Table 3 along with the pertinent parameters for each case. It should be noted that the value of b is determined for flames having the same calculated adiabatic temperature and further assumes that F_v is directly proportional to initial fuel concentration. A review of the values for b listed in Table 3 shows that b varies from approximately 0.4 to 1.5. No systematic variation in b is observed with respect to fuel flow rate. These results can be viewed to be similar to the earlier results of Axelbaum and Law (8-10) who have argued that concentration effects can be of more significance than temperature effects for fuel dilution studies of laminar diffusion flame systems. However, the deviation of b from unity indicates that the dependence on initial fuel concentration could also be complicated by diffusion and residence time effects.

Table 3
Comparison of Fuel Concentration Effect for Flames at Similar Calculated
Adiabatic Flame Temperatures

Fuel	Fuel Flow Rate (cm ³ /s)	T _{AD} (K)	ΔX_F^* %	$\Delta F_v/C(\lambda, m)$ %	b**
C ₂ H ₄	2.75	2313	26	36	1.5
C ₂ H ₄	4.9	2310	26	27	1.06
C ₂ H ₄	4.9	2346	13.5	6.9	0.36
C ₂ H ₄	4.9	2333	18.8	7.6	0.38
C ₂ H ₄	6.58	2333	18.8	15.5	0.81
C ₃ H ₈	2.56	2240	18.0	7.7	0.4

* ΔX_F is based on comparison of Ar and N₂ diluted flames at same calculated temperature.

** b is based on assuming $(\Delta F_v/C(\lambda, m))$ is proportional $(X_F)^b$.

To further examine the effects of fuel dilution, two additional studies were conducted. A series of flames in which a mixture of ethene and toluene were burned in air for different dilution levels was studied. For these studies, the fuel flow rate was held constant at 3.85 and 0.3 cm³/s for ethene and toluene, respectively, while the nitrogen diluent flow rates of 0, 2.1 and 8.4 cm³/s were used. The results of these studies are shown in Table 4. Again the change in concentration is observed to be significantly greater than the observed

variation in soot as measured by ΔF_v . For these toluene studies, the temperature was not held constant and, thus, the observed reduction in soot is due to both temperature and concentration effects.

Table 4

Comparison of Ethene/Toluene Diffusion Flames and High Pressure
Ethene and Propane Flames

Fuel	Fuel Flow Rate (cm ³ /s)	T _{AD} (K)	ΔX_F^*	ΔF_v
C ₂ H ₄ /C ₇ H ₈ /N ₂	3.85/0.3/0	2362	--	--
C ₂ H ₄ /C ₇ H ₈ /N ₂	3.85/0.3/2.1	2333	33.6%	11.9%
C ₂ H ₄ /C ₇ H ₈ /N ₂	3.85/0.3/8.4	2248	67%	36.6%

Fuel	Fuel Flow Rate (cm ³ /s)	T _{AD} (K)	P (atm)	X _F	F _v /c(λ,m) _{max}
C ₂ H ₄	3.85	2369	1	1.0	0.076
C ₂ H ₄	3.85	2351	2	0.5	0.0959
C ₃ H ₈	2.56	2260	1	1.0	0.0490
C ₃ H ₈	2.56	2258	2	0.5	0.0780

	Ratio (F _v /c(λ,m)) _{max}	Ratio X _F
C ₂ H ₄	1.26	.5
C ₃ H ₈	1.59	.5

An alternative method of studying the effect of molecular concentration on growth rate is to alter the concentrations by changing the ambient pressure. The advantage of this approach is to establish a set of flame conditions with a large variation in fuel concentration and only a small temperature variation ($\Delta T < 15$ K). On the other hand, pressure may influence soot formation by other means in addition to concentration modification. Ethene and propane flames at two atmospheres were diluted with argon to an initial molar

fraction of 50%. Since increasing the pressure from one to two atmospheres doubles the concentration of fuel species, the diluted two atmosphere flames have initial fuel concentrations equal to their pure, one atmosphere counterparts. Before making quantitative comparisons between the 1 and 2 atmosphere flames, photographs were taken showing minimal variations in flame size. The peak soot concentrations expressed as $F_v/c(\lambda, m)$ in the 1 and 2 atmosphere ethene flames are 0.076 and 0.096 respectively (see Table 4). In the case of propane, nearly twice as much soot was produced at two atmospheres as compared to one atmosphere (0.049 vs. 0.078). Although the combination of dilution and increased pressure resulted in identical initial fuel concentrations in each flame, the amounts of soot formed increased. Thus, similar to the atmospheric studies, the soot formation process showed a less than first order dependence on concentration when dilution is used to modify the initial concentration conditions.

3.3.5 Discussion

From the above results, it is clear that fuel dilution studies of soot formation can not be interpreted as simple mechanisms involving well controlled overall variations in temperature and concentration. Rather, as with all practical combustion environments, effects of mixing and residence time may be important to consider. In particular, it is important to ascertain how the local concentration and temperature are affected.

The first consideration to be addressed relates to the effects of mixing and asks how diffusion mitigates the effects of the dilution of the fuel. Clearly, when a diluent is introduced, a well defined concentration exists at the fuel tube exits. However, diffusion of species, such as nitrogen from the air flow and combustion products from the reaction zone, begin to alter the concentration. Furthermore, it seems reasonable that the effects of concentration would be most important in the region where soot is formed. To address this question, two activities have been undertaken. The first involves the use of a laminar diffusion flame code by Mitchell et al. (2) to investigate the variation of fuel concentration as a function of position in the flame, while the second involves comparisons with measurements of species profiles in diluted and undiluted flames.

Turning first to the modeling results, Figure 13 shows calculation corresponding to four of the ethene/air flames studied (a) Flames 11 and 1, b) Flames 13 and 9). In this figure, the fuel mole fraction as a function of height along the flame center line is shown. In each case, undiluted or diluted, the fuel mole fractions quickly obtain similar values at axial locations between 10 to 30 mm above the burner exit depending on the fuel flow rate. This effect is a result of the rapid diffusion of nitrogen from the air to the fuel region mitigating the initial dilution. Consequently, all laminar diffusion flames burning in air undergo "dilution" by nitrogen, rapidly reducing the local fuel concentration.

These results are further examined in Figures 14-16 where radial profiles are presented for Flames 11 and 1 at three axial locations (0.3 mm, 2.7 mm and 14.5 mm). Table 5 shows results tabulated for other fuel flow rates at the same axial locations for selected radial positions (4.63 mm and the center line). It is important to note that soot formation is initiated well away from the center line of the flame. Previous results show soot is first observed at a radial location about 5 mm from the center line at an axial location between 3 and 5 mm above the burner for flow conditions typical of the present experiments (12).

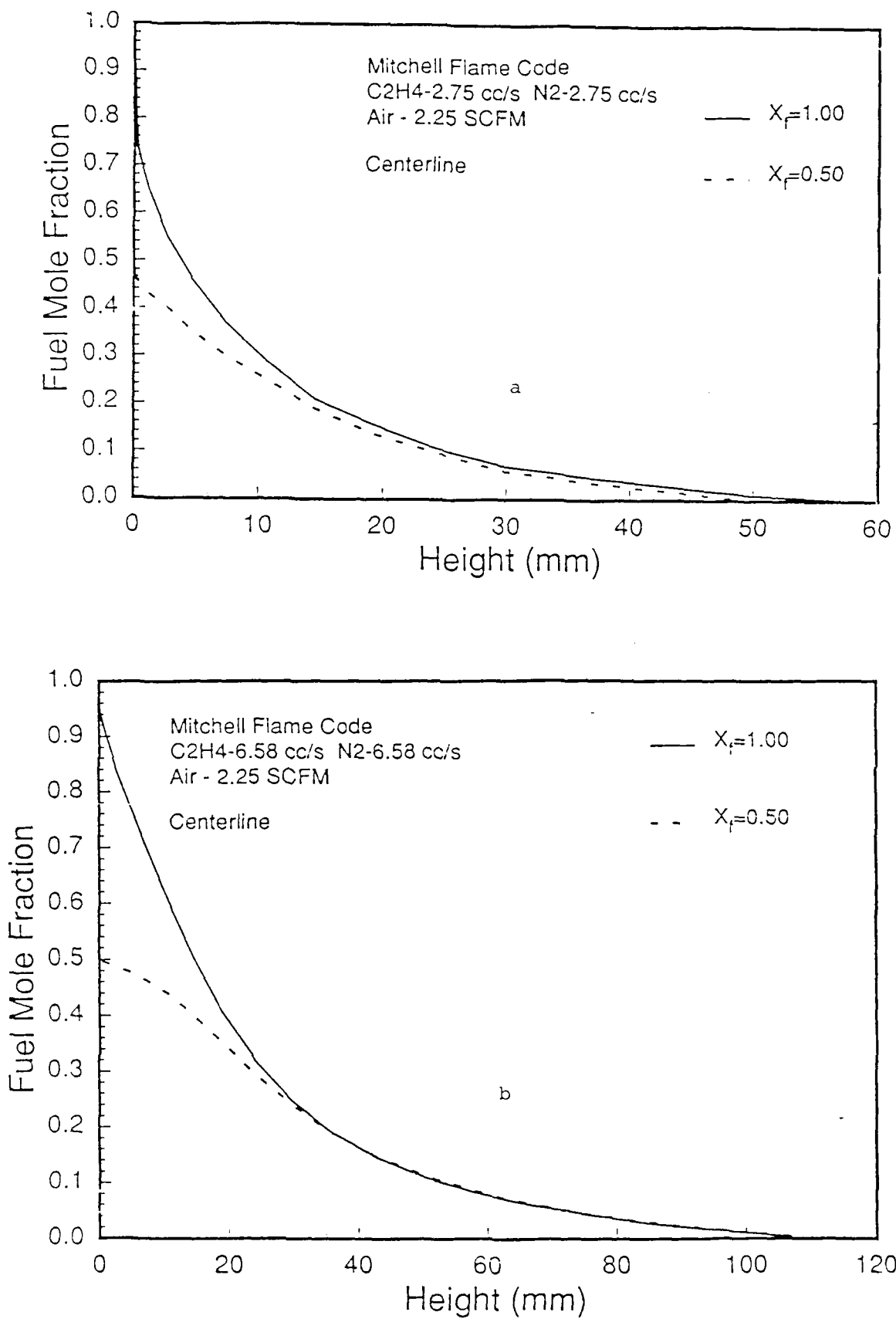


Figure 13. Calculated fuel mole fraction as a function of height above the center line of a diffusion flame for two methane fuel flow rates 2.75 and 6.58 cm³/s. Calculations compare an undiluted and diluted (50% N₂) flame case.

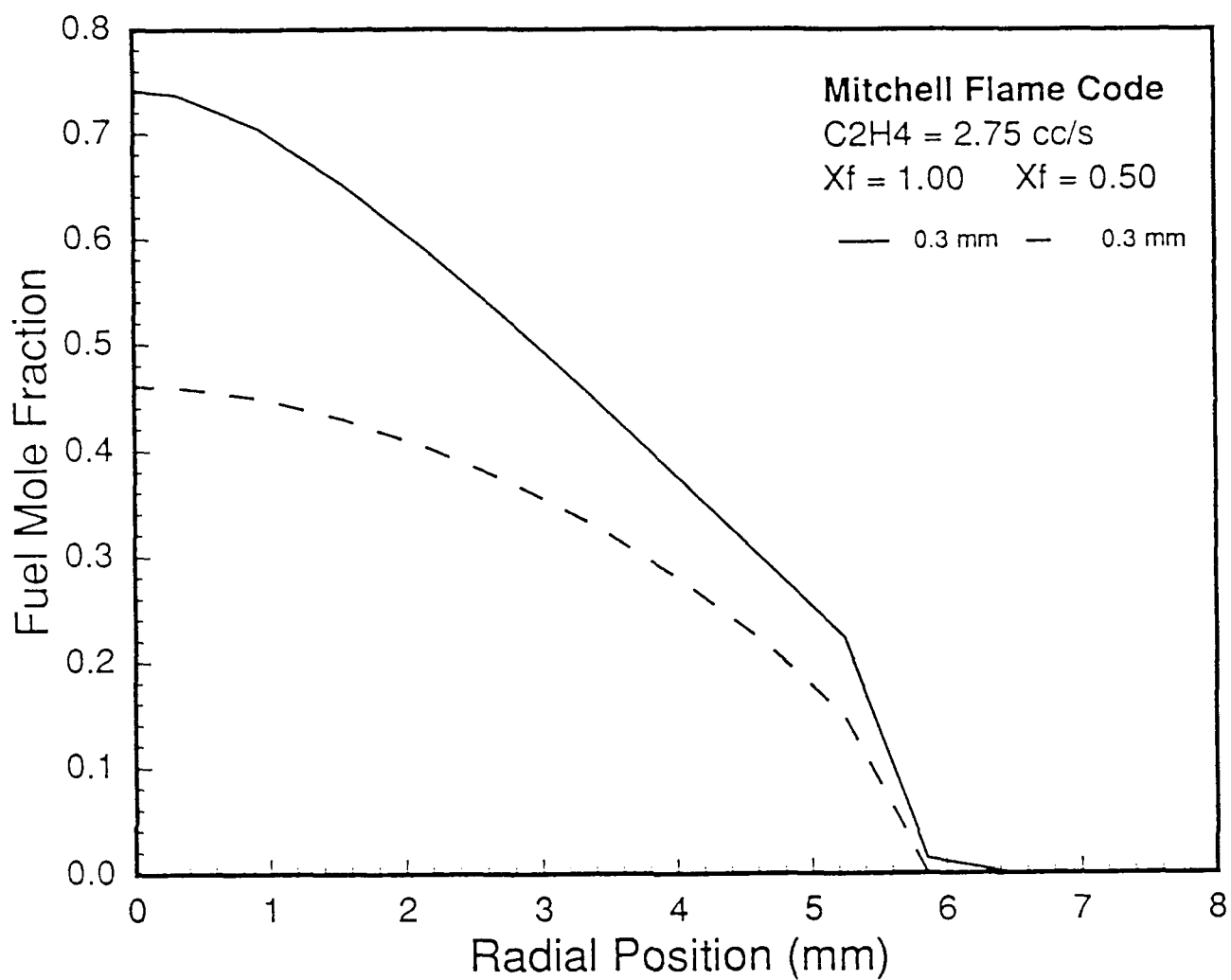


Figure 14. Comparison of the profile of fuel mole fraction as a function of radial position for a diluted and undiluted flame. (axial location - 0.3mm)

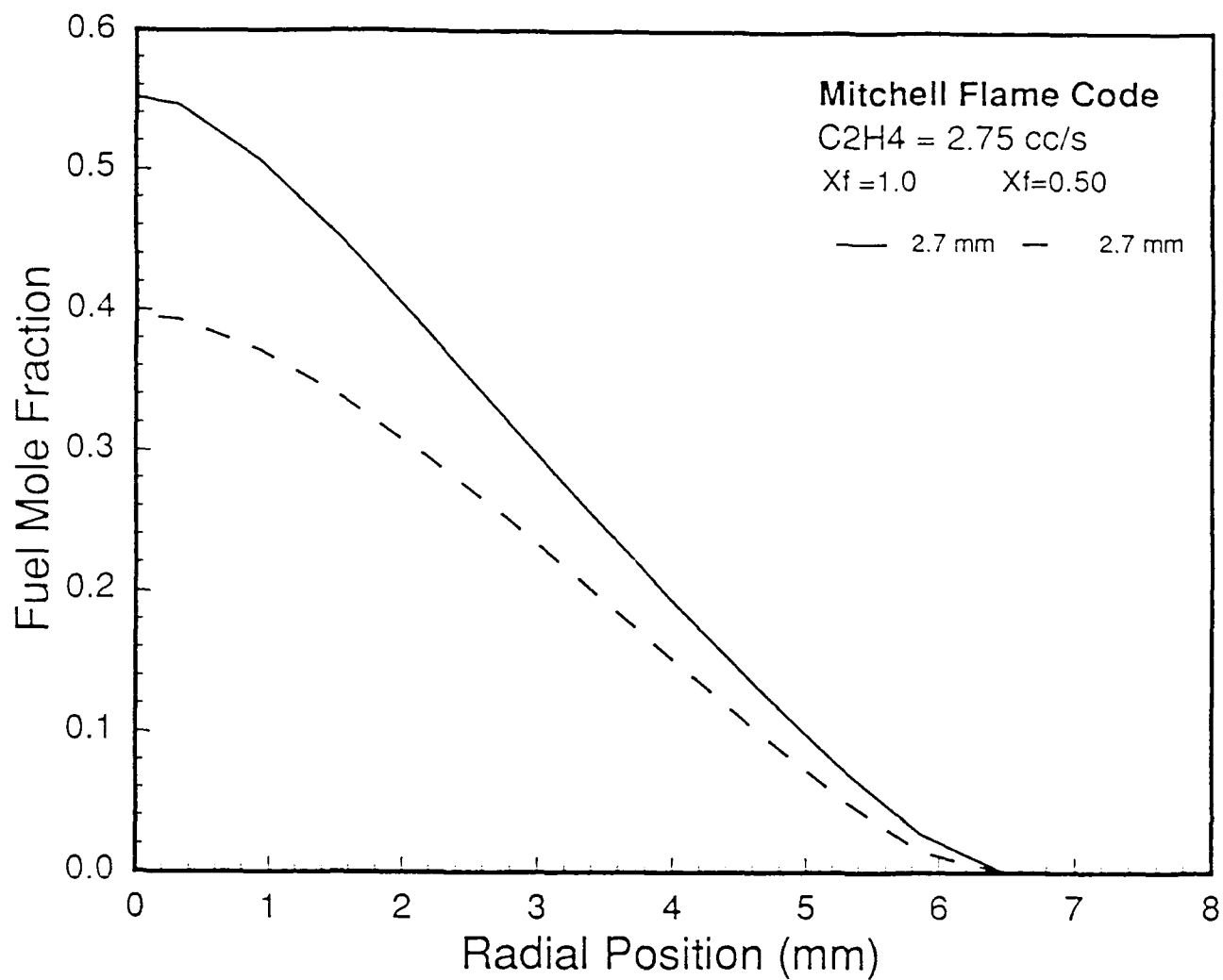


Figure 15. Comparison of the profile of fuel mole fraction as a function of radial position for a diluted and undiluted flame, (axial location - 2.7mm)

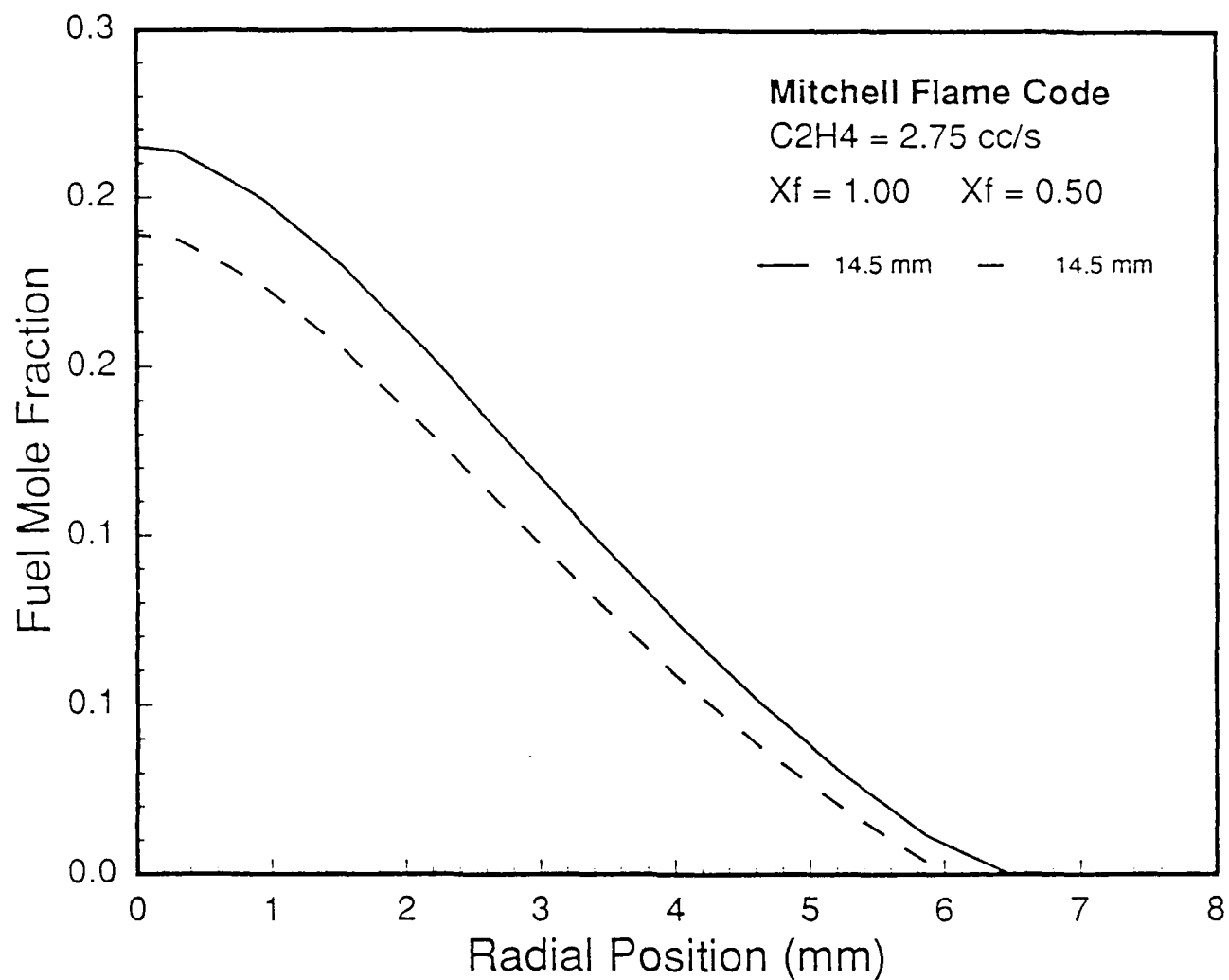


Figure 16. Comparison of the profile of fuel mole fraction as a function of radial position for a diluted and undiluted flame, (axial location - 14.5mm)

Comparisons shown in Table 5 indicate that, in the region where soot is first formed, the local concentration ratio between the diluted and undiluted flame is typically between 0.7 and 0.85. Additionally, the effect of dilution is slightly more pronounced for the lower volumetric fuel flow rate case. At $z = 2.7$ mm and $R = 4.63$ mm, the concentration ratio is 0.76 for the $2.75 \text{ cm}^3/\text{s}$ case as compared to .85 for the $6.58 \text{ cm}^3/\text{s}$ flame.

Table 5
Mitchell Flame Comparisons for Ethene Diffusion Flames

R (mm)	Z (mm)	X_F (Pure)	X_F (50%)	X_F (50%)/ X_F (Pure)	Fuel Flow Rate (cm^3/s)
4.63	0.3	.4824	.3508	.727	6.85
"	2.7	.2561	.2175	.849	"
c.1*	14.5	.5042	.4008	.795	"
4.63	0.3	.4104	.3040	.740	4.9
4.63	2.7	.2068	.1702	.823	4.9
c.1*	14.5	.3833	.3298	.860	4.9
4.63	0.3	.2983	.220	.7375	2.75
4.63	2.7	.1315	.1005	.7642	2.75
c.1*	14.5	.2150	.1889	.8785	2.75

* centerline

From the above results, the effects of dilution of the fuel flow would be expected to be more acute for low fuel flow rate cases and to vary in a smaller than first order manner. Both of these effects are observed in the present experiments (see Table 2).

In order to examine the correspondence of the above modeling results to actual measurements, consider the mass spectrometer measurements presented in Figures 7 and 8 for undiluted and diluted methane flames. These measurements which were obtained at an axial location 12 mm above the burner exit show very similar mole fraction values for CO_2 , O_2 , CH_4 , H_2O and C_2H_2 except in the region near the center line away from where soot is formed. Some differences can be observed for CO and major changes in H_2 are observed. With the exception of H_2 , all the species profiles show results in agreement with the trends discussed above based on the model calculations.

From these results, one can conclude that the local concentration of fuel and combustion products will

quickly achieve similar values in both diluted and undiluted flames. Furthermore, concentration effects, based on initial values at the fuel tube exit, will not reflect the true concentration effects. In addition to these observations, the temperature measurements indicate that dilution does not effect the temperature through the flame in a universal manner. Local temperature variations can be observed in regions where the peak temperatures show good agreement in terms of achieving equivalent "adiabatic" temperature conditions. These local temperature differences, as will be seen shortly, could be responsible for significant variations in the amount of soot formed.

The experimental and modeling results described above have shown that the ratio of the local concentration values in diluted and undiluted flames can be expected to differ significantly from the initial values at the fuel tube exit. In fact, at sufficiently large distances from the burner exit both the diluted and undiluted flames show similar mole fractions for major species. This raises a question regarding what mechanism can be responsible for the variation in soot formation observed for these dilution studies. Two additional effects of particular interest are the temperature and residence time.

Previous work by Kent and Wagner (7) and Bohm et al. (16) indicate that temperature changes of 50K in diffusion or premixed flames can result in a factor of two change in the maximum soot volume fractions observed. In the present flames, comparative differences of approximately 40K are observed in the sooting forming region of the N_2 and Ar diluted flames. The lower temperatures are observed for the Ar diluted case which exhibit the lower soot formation rates. Consequently, temperature effects could be more pronounced than originally anticipated for flames which have equal adiabatic flame temperatures. These results, again, point to the need for local measurements to properly examine effects based on overall variations of the initial conditions of the diffusion flame.

Residence time effects have also been shown to be important in diffusion flame studies of soot formation (17,18). In fact, a squared or cubed power dependence on the residence time has been observed (18). Thus, changes in the velocity which result from addition of the diluent species could affect the residence time and the soot formation rate as a result. However, the major observed effect of dilution with respect to residence time is a shift of the location where soot is first observed to higher axial positions. Since the location of the maximum soot volume fraction is largely unaffected by dilution, the total soot residence time is reduced. Note the shift in the location of the initial soot formation region could be a result of temperature, velocity and/or concentration effects. Our preliminary evaluation of this effect estimates that between 5 to 20% of the reduction in soot could be a result of the variation in residence time during which soot growth can occur. These studies will be refined in the near future to better characterize the onset location of soot formation as a function of dilution, since this has proved to be a point of some interest.

3.3.6 Conclusions

The present study of the effects of fuel dilution on soot formation in laminar diffusion flames indicates a number of important effects are present. The lower soot formation rate observed is due to a combination of concentration, temperature and residence time effects. Based on local measurements of the temperature

variations in the soot forming regions of the flame, along with previous measurements of the sensitivity of the soot formation process to temperature variation, we argue that temperature is still the most important effect. Our measurements and modeling show that concentration effects are mitigated by diffusional processes associated with the diffusion flame structure. In particular, diffusion of nitrogen from the surrounding air quickly results in similar concentration fields for both diluted and undiluted flames. Furthermore, dilution appear to increase the time for soot particle inception to occur, resulting in a decreased residence time for soot growth. This effect can only account for between 5 and 20% of the observed change in soot formation, but in conjunction with other effects should be taken into account.

Our studies indicate that concentration effects can be responsible for some fraction of the observed variation in soot formation as diluent is added. These effects are most important in the soot inception region and appear to decrease in importance as residence time and sooting propensity increase. Additionally, the present studies point to the usefulness of detailed studies to investigate fundamental mechanisms involving soot formation as opposed to global studies.

4.0 Future Work

During the next year of the research effort, emphasis will be given to applying the EMS probe and mass spectrometer system to measurements in the particle inception and particle growth region. In the particle inception region, measurements of high mass species will be of particular interest and attempts to link these measurements to earlier fluorescence studies of the particle inception process will be pursued. In the surface growth region, acetylene measurements are of most interest, since this species is often argued to be the key surface growth reactant.

Efforts will also continue in the study of high pressure flames where they complement present studies as demonstrated in the previous section. Work on extending some of the previous high pressure flame studies of alkane fuels to ten atmospheres is planned to complete the comparison between the alkene and alkane fuels. These high pressure flame studies have not been pursued during the past year because of the emphasis given to the concentration studies. Finally, efforts to provide a review article on soot formation processes will be undertaken. Recent work from this laboratory as well as others warrant that a new review of the field be provided.

5.0 References

1. Puri, R. and Santoro, R. J., "Sonic Probe Sampling in Particle Laden Combustion Flows", The Fall Technical Meeting, Eastern Section: The Combustion Institute, Orlando, FL, December 3-5, 1990.
2. Mitchell, R. E., Sarofim, A. F. and Clomburg, L. A., "Experimental and Numerical Investigation of Laminar Diffusion Flames", Combustion and Flame, 37, pp. 227-244 (1980).
3. Smyth, K. C., Miller, J. H., Dorfman, R. C., Mallard, W. G. and Santoro, R. J., "Soot Inception in a Methane/Air Diffusion Flame as Characterized by Detailed Species Profiles", Combustion and Flame, 62, pp. 57-181 (1985).
4. Deardon, P. and Long, R., "Soot Formation in Ethylene and Propane Diffusion Flames", J. Appl. Chem., 18 (1968).
5. Glassman, I. and Yaccarino, P., "The Temperature Effect in Sooting Diffusion Flames", Eighteenth Symposium (International) on Combustion, The Combustion Institute, p 1175 (1981).
6. Santoro, R. J. and Semerjian, H. G., "Soot Formation in Diffusion Flames: Flow rate, Fuel Species, and Temperature Effects", Twentieth Symposium (International) on Combustion, p. 997 (1984).
7. Kent, J. H. and Wagner, H. G., "Why Do Diffusion Flames Emit Smoke?", Combust. Sci. and Tech., 41, p. 245 (1984).
8. Axelbaum, R. L., Flower, W. L. and Law, C. K., "Dilution and Temperature Effects of Inert Addition on Soot Formation in Counterflow Diffusion Flames", Combust. Sci. and Tech., 61, p. 51 (1988).
9. Axelbaum, R. L., Law, C. K. and Flower, W. L., "Preferential Diffusion and Concentration Modification in Sooting Counterflow Diffusion Flames", Twenty-Second Symposium (International) on Combustion, The Combustion Institute, p. 379 (1988).
10. Axelbaum, R. L. and Law, C. K., "Soot Formation and Inert Addition in Diffusion Flames", The Twenty-third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, (in press).
11. Gordon, S. and McBride, B. J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks and Chapman-Jouguet Detonations", NASA SP-273, Interim Revision N78-17724, March 1976.
12. Santoro, R. J., Semerjian, H. G. and Dobbins, R. A., "Soot Particle Measurements in Diffusion Flames", Combust. and Flame, 51, 203 (1983).
13. Roper, F. G., "The Prediction of Laminar Jet Diffusion Flame Sizes: Part I. Theoretical Model.", Combust. and Flame, 29, 219 (1977).
14. Boedeker, L. R. and Dobbs, G.M., "CARS Temperature Measurements in Sooting, Laminar Diffusion Flames", Combust. Sci. and Tech., 46, 301 (1986).
15. Roper, F. G., Smith, C. and Cunningham, A. C., "The Prediction of Laminar Jet Diffusion Flame Sizes: Part II. Experimental Verification". Combust. and Flame, 29, 227 (1977).
16. Bohm, H., Hesse, D., Jander, H., Luers, B., Pietscher, J., Wagner, H. Gg. and Weiss, M., "The Influence of Pressure and Temperature on Soot Formation in Premixed Flames", The Twenty-second Symposium (International) on Combustion, The Combustion Institute, pp.403-411 (1988).

17. Santoro, R. J., Yeh, T. T., Horvath, J. J. and Semerjian, H. G., "The Transport and Growth of Soot Particles in Laminar Diffusion Flames", *Combustion and Technology*, 53, p. 89 (1987).
18. Honnery, D. R. and Kent, J. H., "Soot Formation in Long Ethylene Diffusion Flames", *Combustion and Flame*, 82, pp. 426-436 (1990).

6.0 Publications

1. Santoro, R. J., Yeh, T. T., Horvath, J. J. and Semerjian, H. G., "The Transport and Growth of Soot Particles in Laminar Diffusion Flames," Combustion Science and Technology, 53, 89 (1987).
2. Solomon, P. R., Best, P. E., Carangelo, R. M., Markham, J. R., Chien, P., Santoro, R. J. and Semerjian, H. G., "FT-IR Emission/Transmission Spectroscopy for In-Situ Combustion Diagnostics", Twenty-first Symposium (International) on Combustion, The Combustion Institute, pp. 1763-1771 (1986).
3. Santoro, R. J. and Miller, J. H., "Soot Particle Formation in Laminar Diffusion Flames", Langmuir, 3, p. 244-254 (1987).
4. Santoro, R. J., "Optical Measurements of Soot Particles in Flames," Mat. Res. Soc. Symp. Proc., Vol. 117, p. 157 (1988).
5. Dobbins, R.A., Santoro, R.J. and Semerjian, H.G., "Analysis of Light Scattering from Soot Using Optical Cross Sections for Aggregates". Twenty-Third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, in press.
6. Davis, R.W., Moore, E.F., Santoro, R.J. and Ness, J., "Isolation of Buoyancy Effects in Jet Diffusion Flames", Combustion Science and Technology, 73, pp. 625-635 (1990).
7. Santoro, R. J., "Coagulation in Soot Formation in Combustion", An International Round Table Discussion, H. Jander and H.Gg. Wagner (eds), Vandenhoeck and Ruprecht, Göttingen, 1990.

7.0 Meetings and Presentations

1. "The Effect of Fuel Structure on the Formation and Growth of Soot Particles in Diffusion Flames," The Twenty-third Biennial Conference on Carbon, Worcester Polytechnic Institute, July 19-24, 1987.
2. "Soot Particle Formation in Diffusion Flames," American Chemical Society Symposium on Advances in Soot Chemistry, ASC Symposium, New Orleans, LA, August 30-September 4, 1987.
3. "Fuel Molecular Structure Effects on Soot Particle Growth in Diffusion Flames", Twentieth Fall Technical Meeting of the Eastern Section of the Combustion Institute, Gaithersburg, MD, November 2-5, 1987.
4. "Optical Measurements of Soot Particles in Flames," Materials Research Society Symposia, Reno, Nevada, April 5-8, 1988.
5. "Soot Growth in Diffusion Flames Burning Fuel Mixtures," 1988 Fall Technical Meeting of the Eastern Section of the Combustion Institute, Clearwater Beach, FL, December 5-7, 1988.
6. "Optical Measurements of Soot Particles in Flames," Wright Patterson Air Force Base, Dayton, Ohio, March 6, 1989.
7. Invited Attendee for the Round Table Discussion on "Current Problems in Soot Formation During Combustion," The Commission on Condensation Phenomena of the Academy Science, Gottingen, Germany, March 29 and 30, 1989.
8. Invited Tutorial on Particle Diagnostics, 1989 Annual Meeting of the American Association for Aerosol Research, Reno, Nevada, October 9, 1989.
9. "Surface Growth and Coagulation Processes in Soot Particle Formation," AIChE Annual Meeting, San Francisco, CA, November 6-10, 1989.
10. "Isolation of Buoyancy Effects in Jet Diffusion Flames," presented at the 1990 Central States Section of the Combustion Institute, Cincinnati, OH, May 20-22, 1990.
11. "Two-Dimensional Imaging Techniques for Particle Size Characterization", Twenty-First Annual Meeting of the Fine Particle Society, San Diego, CA, Aug. 21-25, 1990.
12. "An Application of Two-Dimensional Imaging Techniques for Soot and Droplet Studies", 1990 ASME Winter Annual Meeting, The Symposium on Heat and Mass Transfer in Fire and Combustion Systems, Dallas, TX, Nov. 25-30, 1990.
13. "The Effect of Inert Diluent Addition on Diffusion Flame Height in an Oxygen Atmosphere", 1990 Fall Technical Meeting, Eastern Section of the Combustion Institute, Orlando, FL, Dec. 3-5, 1990.
14. "Sonic Probe Sampling in Particle Laden Combustion Flows", 1990 Fall Technical Meeting, Eastern Section of the Combustion Institute, Orlando, FL, Dec. 3-5, 1990.

8. Participating Professionals

Dr. Robert J. Santoro, Associate Professor of Mechanical Engineering

Mr. Rahul Puri, Graduate Student, Department of Mechanical Engineering (Ph.D. expected 12/91).

Mr. Jeff Leet, Graduate Student, Department of Mechanical Engineering (M.S. completed 8/90, presently employed at Southwest Research Institute)

Mr. Thomas Richardson, Graduate Student, Department of Mechanical Engineering (Ph.D. expected 12/91).

Mr. John Ness, Graduate Student (AFRAPT), Department of Mechanical Engineering (M.S. employed at David Taylor Laboratory)

Mr. Robert Burch, Graduate Student (AFRAPT), Department of Mechanical Engineering

Mr. Darrell Rapp, Graduate Student (AFRAPT), Department of Mechanical Engineering (Ph.D. expected 12/93).

Ms. Yamilla Cancel-Sanchez, Undergraduate Student, Department of Chemical Engineering (B.S. 6/93).

9. Interactions

A number of researchers have directly used the extensive data set developed as part of this work to compare with or extend their own research. Some of those who have been directly provided data include:

Professor R. A. Dobbins, Brown University, Providence, RI
Dr. R. Hall, United Technologies Research Center, East Hartford, CT
Dr. R. Davis, The National Bureau of Standards, Gaithersburg, MD
Dr. P. Solomon, Advanced Fuel Research, Inc., East Hartford, CT
Dr. I. Kennedy, University of California, Davis, CA
Drs. C. Merkle and S. Turns, The Pennsylvania State University, University Park, PA
Dr. H. Mongia, Allison Gas Turbine Division-GM, Indianapolis, IN

In addition to the interactions resulting from interest in the soot particle data, there have been interactions with researchers on particle diagnostic problems. In some cases this has resulted in direct visits to particular laboratories to assist in solving these problems. These interactions include:

Dr. M. Zachariah, The National Institute of Standards and Technology, Gaithersburg, MD
Dr. Valerie Lyons, NASA-Lewis Research Center, Cleveland, OH

Several other interactions have also occurred through a general interest in the work supported by AFOSR with:

Columbian Chemical Company, Monroe, LA
Cummins Engine Company, Columbus, IN
E. I. DuPont de Nemours, Wilmington, DE
Eastman Kodak, Rochester, NY
Allison Gas Turbine Division

DuPont is currently supporting work on titanium dioxide particle formation as a direct result of the AFOSR research program. A student, Peter Strakey, will spend the summer with DuPont exchanging expertise and technology developed as part of this research.

Recent work with Allison Gas Turbine Division involving the incorporation of a revised soot model in the gas turbine combustion codes is proceeding. Mr. Darrell Rapp who is an AFRAPT participant is spending summers working at Allison on the implementation of that model. This work is an attempt to directly transfer the results of our work to industry.